California Environmental Protection Agency

Air Resources Board

Monitoring and Laboratory Division
Air Quality Surveillance Branch

Sampling Protocol for 1, 3-Dichloropropene, Methyl Bromide, Chloropicrin and Methyl Iodide Application Monitoring

6 August, 2010

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Signatures:

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The following protocol has been reviewed and approved by staff of the Air Resources Board (ARB). Approval of this protocol does not necessarily reflect the views and policies of the ARB, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

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1.0 Introduction

At the request of the California Department of Pesticide Regulation (DPR), January 4, 2010 Memorandum, Reardon to Goldstene the Air Resources Board (ARB) staff will monitor ambient air concentrations for 1,3-dichloropropene (1,3-D), methyl bromide (CH_3Br), chloropicrin (Cl_3CNO_2) and methyl iodide (CH_3I). This ambient air monitoring study will be performed at sites close to communities of higher population density near areas with high use of 1,3-D and CH_3Br. Chloropicrin is a fumigant contained in most 1,3-D and methyl bromide products. This ambient air monitoring study is requested by DPR to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5, Section 14022(c)) which requires the ARB "to document the level of airborne emissions…. of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of methyl iodide as a selective preplant soil fumigant.

The laboratory analysis method titled the “SOP MLD 058 Standard Operating Procedure for the Determination of Aromatic and Halogenated Compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry” Revision 2.00, dated May 15, 2002 is included as Appendix A. The “Standard Operating Procedure Sampling and Analysis of Trichloronitromethane (Chloropicrin)” Revision 3, dated July 14, 2004, is included as Appendix B.

2.0 Project Goals and Objectives

The goal of this monitoring project is to collect and measure 1,3-D, CH_3Br, CH_3I and Cl_3CNO_2 in ambient air during a 15 month period.

To achieve the project goal, the following objectives should be met:

1. Appropriate use of sampling/monitoring equipment to determine ambient 1.3-D, CH_3Br, CH_3I and Cl_3CNO_2 concentrations at two sites requested by DPR.

2. Application of relevant quality control practices to ensure the integrity of field samples.

3. At the conclusion of the project, MLD will provide DPR with a final report containing all relevant data for this project.

3.0 Contacts

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4.0 Study Location and Design 1,3-D, CH_3Br, CH_3I and Cl_3CNO_2

The compound 1,3-dichloropropene (1,3-D) is a preplant soil fumigant used primarily for controlling all major species of nematodes including root knot, lesion, stubby root, dagger, ring, and cyst nematodes. The compound methyl bromide (CH_3Br) is used as a fumigant against insects, termites, rodents, weeds, nematodes, and soil-borne diseases. The compound chloropicrin (Cl_3CNO_2) is used as a fumigant to control pests found in the soil and is commonly used in combination with other fumigants, such as CH_3Br. The fumigant methyl iodide (CH_3I) is a preplant biocide used primarily for controlling insects, plant parasitic nematodes, soil borne pathogens and weed seeds, and is proposed to be used as a replacement for CH_3Br. The Department of Pesticide Regulation (DPR) recently approved several field research studies of this pesticide although it has not been registered for use in California. In the event DPR registers CH_3I, they expect use to be high, and might request further extensive monitoring.

Study Location

The DPR requested the Air Resources Board (ARB) to monitor two (2) communities; one (1) community in Santa Barbara County and one (1) community in Ventura County. The ARB's air quality monitoring station located at 906 S. Broadway, Santa Maria, CA, will be used for the Santa Barbara County location (Figure 1). The Ventura County location will be the County of Ventura Animal Services facility, 600 Aviation Drive, Camarillo, CA. 93010 (Figure 2).

Figure 1
ARB Santa Maria – South Broadway
906 S. Broadway, Santa Maria, Ca.

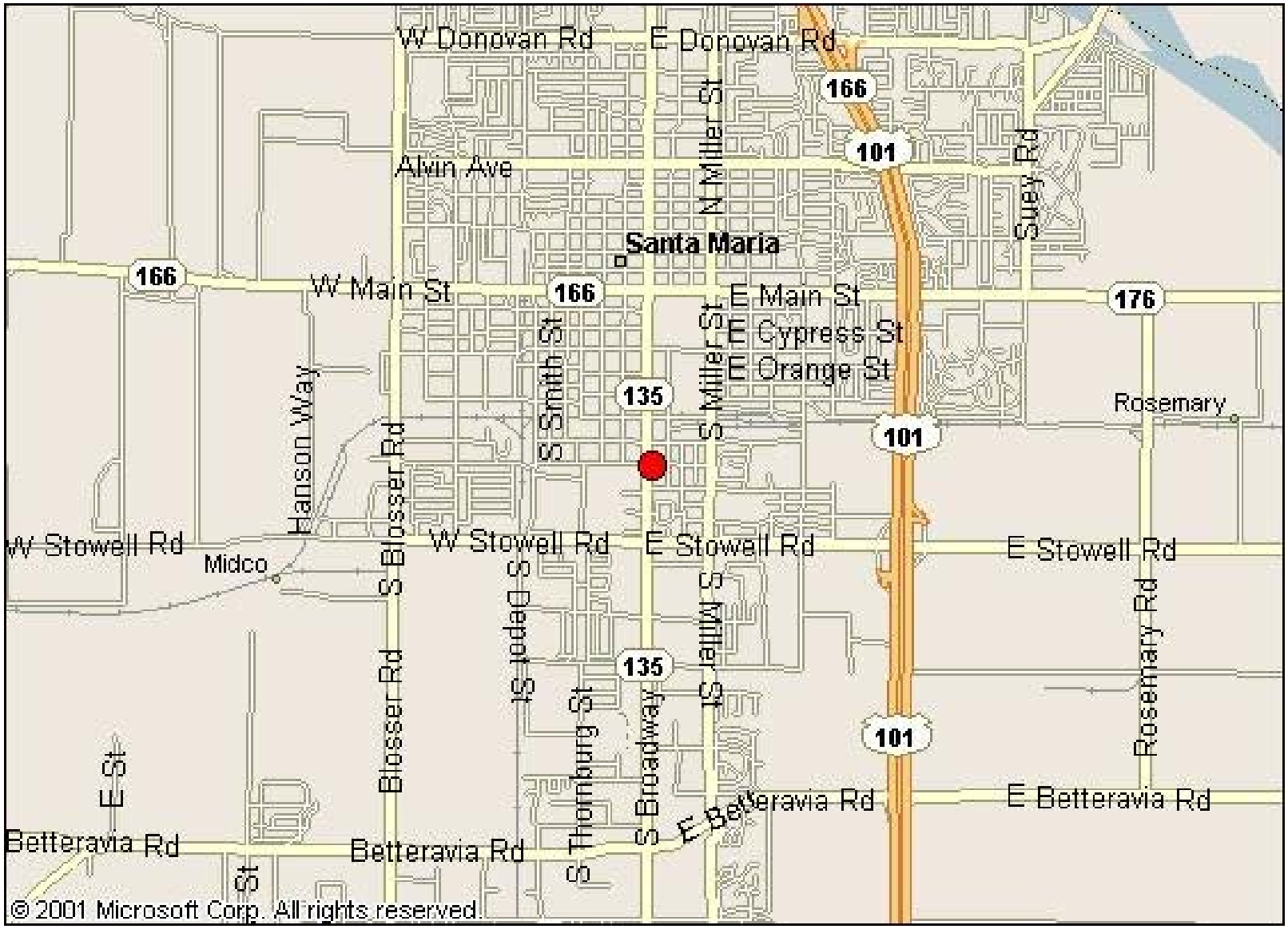
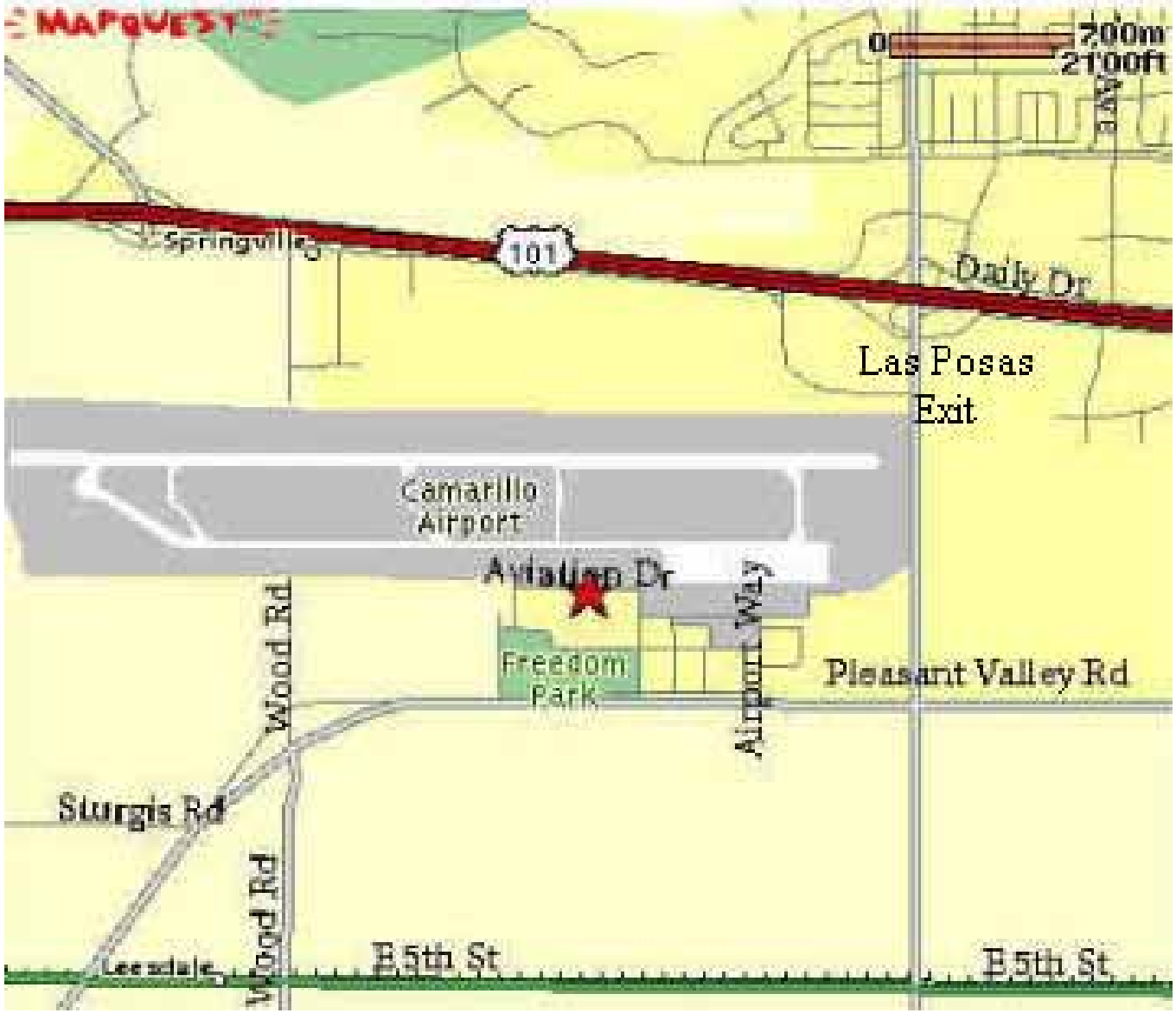


Figure 2
Animal Services, County of Ventura
600 Aviation Drive, Camarillo, Ca. 93010



Study Design

The ARB and the DPR will conduct the ambient air monitoring utilizing two different methods: Tisch TE-323 Samplers with canisters for 1,3-dichloropropene (1,3-D), methyl bromide (MeBr), and methyl iodide (MeI) and mini-vols with sorbent tubes for chloropicrin (Cl_3CNO_2). Samples will be collected at the two (2) locations selected for periods of 24 hours. The sample times and dates are to be determined to conform to the site operators schedule. The weekly sample days will be varied so more than one weekday is sampled throughout the study. The weekly sample days at both sites may not coincide.

Sampling Method

The method using the Tisch canister sampler enables field staff to program equipment for unattended start and stop activation. The sampler can accommodate up to three (3) canisters for unattended sequential sampling. Canisters can be filled up to one (1) atmosphere above ambient pressure. The target final canister pressure is 10 psig, ±5 psig. If the final canister pressure is above 15 psig, the sample will be flagged. If the final canister pressure is below 5 psig, the sample will be invalidated. Samples will be collected by pressurizing ambient air into a Summa canister. The sampling period is 24 hours. A volume of air is pulled through the Tisch TE-323 inlet. By adjusting a turn style valve, a regulated portion of the air (approximately 7.8 ccm) from the inlet goes into the sample canister. The inlet heights will be placed at approximately 1.5 meters above the ground. The Santa Maria site will have three (3) Tisch samplers. One (1) is a primary sampler that will sample once per week. The second is for once per month collocated samples. The third sampler will be operated once per month to perform quality control samples (spikes and/or blanks).

The second method will consist of a mini-vol sampler, which have the capability for staff to program start and stop times for the pump. The flow is regulated by a variable flow valve and a bypass valve. The measured ambient air is pulled through a sorbent (XAD-4). The Santa Maria site will have three (3) of these samplers. Having the same schedule as the canister method, there will be one (1) primary sampler, one collocated sampler (monthly) and one (1) spike/blank. The sample times and dates will conform to the site operators schedule. The collocated, spike and blank samples will be initially collected with the assistance Special Purpose Monitoring staff.

The samples will be analyzed by the Northern Laboratory Branch, Organics Laboratory Section's canister method titled SOP "MLD 058 Standard Operating Procedure for the Determination of Aromatic and Halogenated compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" (Appendix A) and sorbent tubes will be analyzed by the Northern Laboratory Branch, Special Analysis Section's "Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (Appendix B).

Every attempt will be made to shield all sampled canisters and XAD resin cartridges from direct sunlight to help reduce potential losses for the compounds of interest. Canister samples will be removed from the samplers and shipped back to the

Northern Laboratory Branch, Special Analysis Section in Sacramento. The Cl_3CNO_2 samples will be removed from the samplers and immediately placed in provided cold blue ice containers for shipping. The Cl_3CNO_2 samples will be shipped as soon as possible to the Northern Laboratory Branch, Special Analysis Section in Sacramento.

TABLE 1: Guidelines for Sampling Schedule

Sample period:	Sample duration time:
Weekly Canister	2 canister per week/24 hours each (1 per site)
Monthly Canister (Collocated)	1 canister per month – 24 hours each
Monthly Canister (Spike)	1 canister per month – 24 hours each
Monthly Canister (Blank)	1 canister per month – 24 hours each

TABLE 2: Number of Canisters needed (These canisters are to be shipped as needed throughout the 15 month study period)

Canister Type:	Total Number of Canisters needed:
Ambient Samples	**130 canisters** (total) 65 per site
Collocated Samples	**15 canisters** (total) Santa Maria
Spikes	**15 canisters** (total) Santa Maria
Blanks	**15 canisters** (total) Santa Maria

Figure 3
The Camarillo Enclosure
with
Tisch TE-323 Canister Sampler and Mini Vol Sorbent Tube Sampler

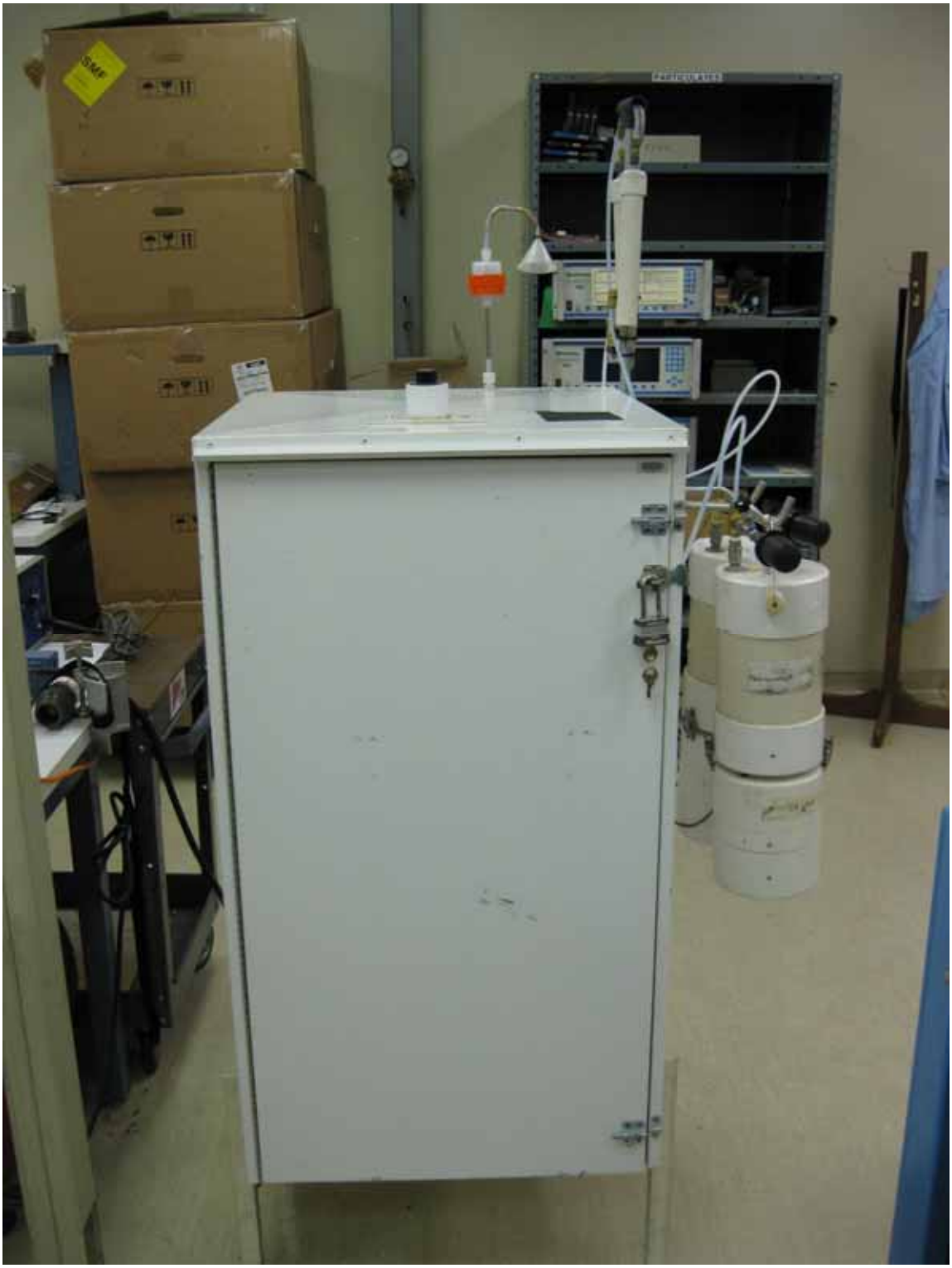


Figure 4
The Camarillo Enclosure Open
with
Tisch TE-323 Canister Sampler with Summa Canister
And Mini Vol Sorbent Tube Samplers

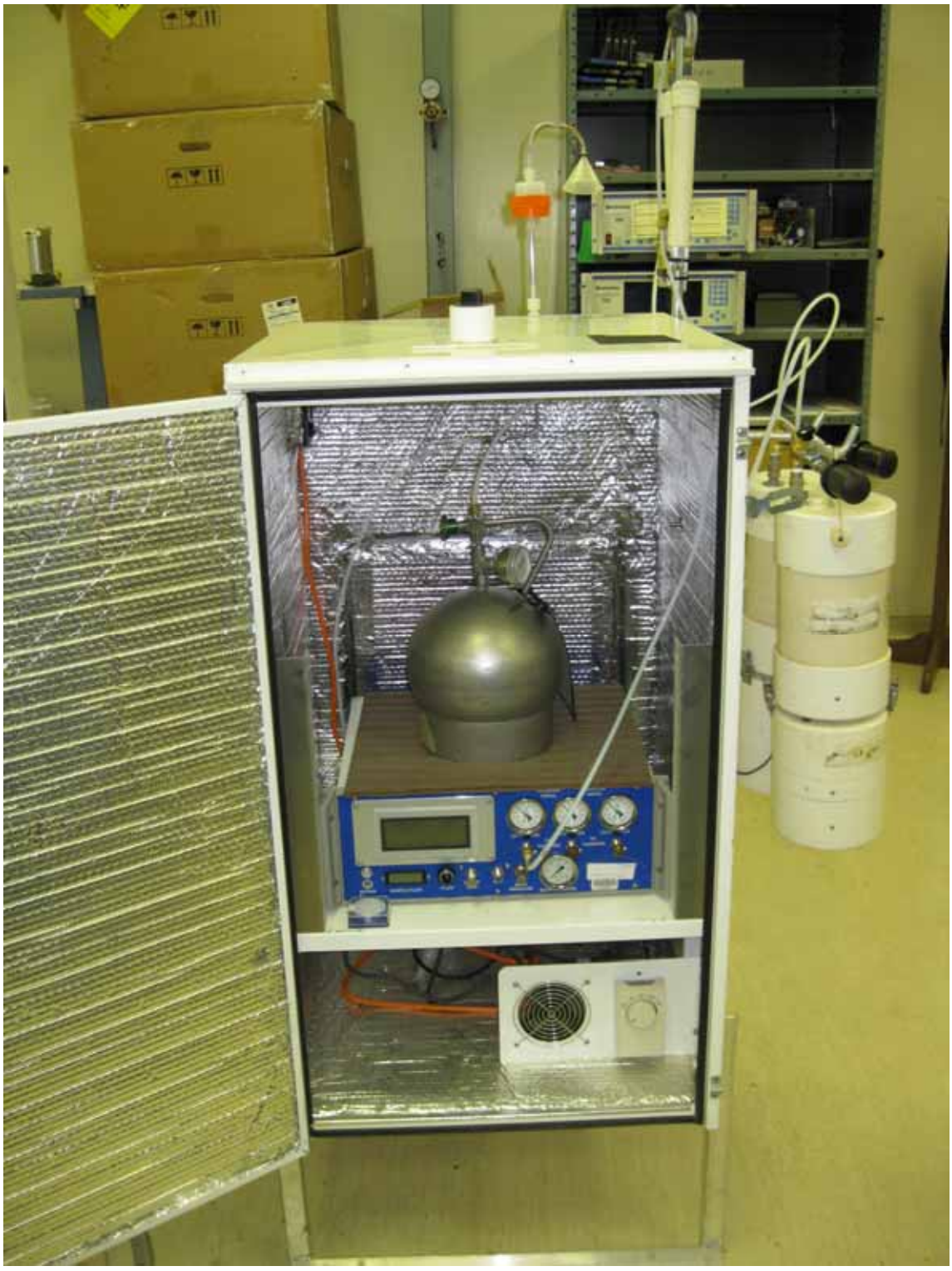


Figure 5
The Santa Maria Mini Vol Sorbent Tube Samplers

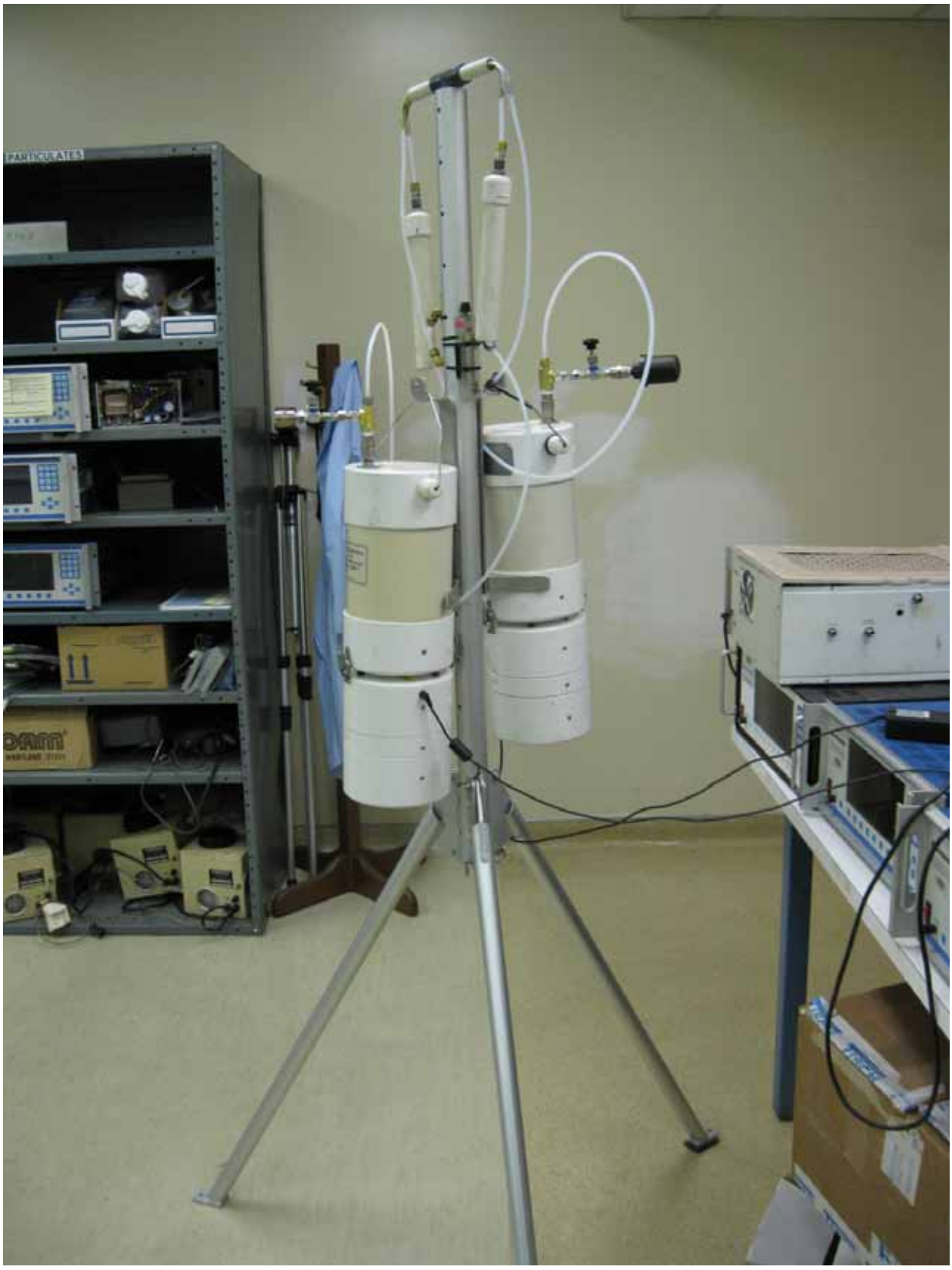
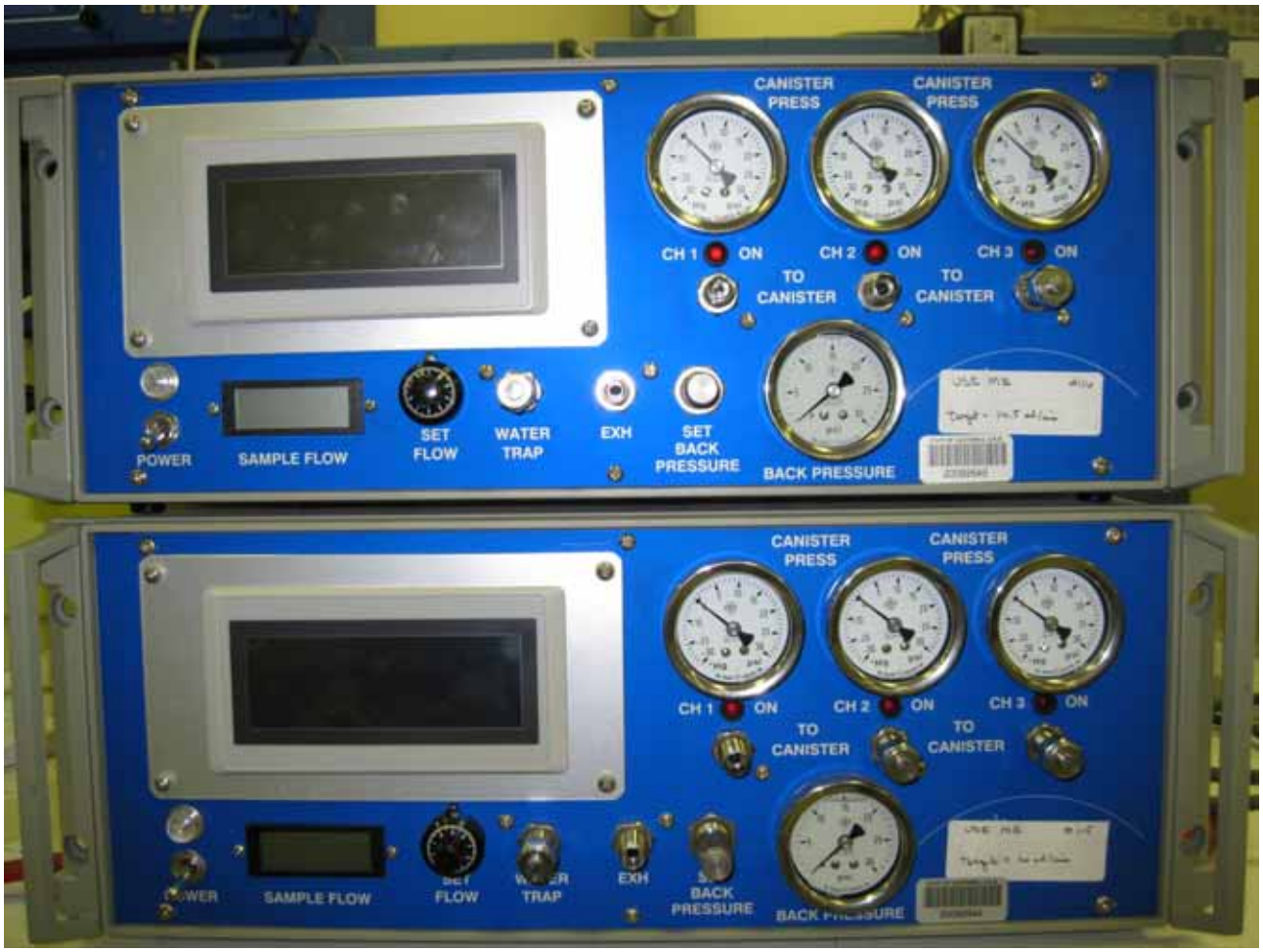


Figure 6
The Santa Maria
Tisch TE-323 Canister Samplers



5.0 Sampling and Analysis Procedures

A log book will be maintained by field staff at each site.

Canister Sampling: The Monitoring and Laboratory Division's Organics Laboratory Section will provide Special Purpose Monitoring and/or field staff with cleaned and evacuated Summa canisters, in addition to preparing the necessary spiked canisters. These samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

Prior to removing each sampled canister from the sampler, the operator will assure that the canister valve is securely closed and the corresponding sample paperwork is complete. The collected canisters will be shipped as soon as possible back the Laboratory. When received by the Laboratory, the canister samples will be analyzed as soon as possible.

All reported sampling times, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch, Organics Laboratory Section's canister method is titled "SOP MLD 058 Standard Operating Procedure for the Determination of Aromatic and Halogenated compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry" (Appendix A).

Sorbent Tube Sampling: The Monitoring and Laboratory Division's Special Analysis Section has provided sorbent tubes to the Special Purpose Monitoring section. During the duration of this study, the laboratory will also provide spiked sorbent sample tubes to field staff. Spikes will be shipped at the appropriate temperature. These samples will not be exposed to extreme conditions or subjected to rough handling that might affect sample integrity.

The operator will remove the sorbent tubes immediately following the completion of the sampling period and will place samples into the prepared blue ice shipping container. All corresponding sample paperwork will be completed at this time. The samples will be shipped as soon as possible back the Laboratory. When received by the Laboratory, the canister samples will be analyzed as soon as possible.

All reported sampling times, will be reported in Pacific Standard Time (PST).

The Northern Laboratory Branch, Special Analysis Section's sorbent tube method is titled "Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (Appendix B).

The following canister/sorbent tube validation and analytical quality control criteria should be followed during pesticide analysis.

1. **Sample Hold Time**: Sample hold time criteria will be established by the Laboratory. Samples not analyzed within the established hold time will be invalidated by the Laboratory.

2. **Duplicate Analysis**: Laboratory to establish relative percent difference (RPD) criteria for duplicate analysis. Laboratory will also provide duplicate analytical results and RPD.

3. **Method Detection Limit (MDL)**: MDL sample analytical results less than the MDL shall be reported as a less than numerical value. This less than numerical value shall incorporate any dilutions/concentrations.

4. **Analytical Linear Range**: Any analytical result greater than the highest calibration standard shall be reanalyzed within the calibrated linear range.

6.0 List of Field Equipment

Quantity	Item Description
(1)	Global Positioning System (GPS) with backup batteries and carrying case
(1)	Digital Camera with backup batteries and carrying case
(2)	Alborg mass flow meter 0-20 cc/min
(2)	Alborg mass flow meter 0-200 cc/min
(1)	Tisch TE-323 canister samplers (Camarillo)
(3)	Tisch TE-323 canister samplers (Santa Maria)
(6)	Sampling inlets (from Tisch to canister)
(6)	Inlet tubing with particulate filter
(120)	Spare particulate filters (two sites/one per month/15 months/4 samplers)
(1)	Enclosures to protect Tisch sampler
(175)	Summa canisters (See Table 2 – 145 clean (including collocated), 15 spikes, 15 blanks)
(95)	Sample sheets for each canister
(6)	Mini Vols with connectors, tubing and weather/sun shields
(12)	Mini Vol batteries with chargers
(2)	Extension cords
(1)	Tripod for mini Vols at Santa Maria
(1)	Zero air cylinder for blanks from Santa Maria
(15)	Set of spikes to be collected from Santa Maria (canister & sorbent)
(1)	Weed eater for Camarillo
(10)	Shipping boxes with blue ice packs

[Place data sheet inside plastic pouch]

CALIFORNIA AIR RESOURCES BOARD
SILCO Canister Pesticide Data/Sample Tracking Sheet

Pesticides
Tisch
Sampler

Project Name: _____

Site/Sample Name: _____

Lab I.D.: _____ Operator & Agency: _____

			CANISTER		LABORATORY	SAMPLER			
	Date	Time (PST)	Vacuum ("Hg)		Pressure or Vacuum	MFC Reading		Vacuum	
			LAB	FIELD					
Set-Up									
Start									
Stop					LAB**				

Type of Sample: [ ] Regular [ ] Collocated [ ] Spike [ ] Blank [ ] Other

Field Log Number: _____ Canister ID Number: _____ Sampler ID Number: _____

Observed Unusual Sampling Condition: [ ] Wind-Blown Sand/Dust [ ] Rain /Fog/Elevated Humidity [ ] Farming Nearby [ ] Construction Nearby [ ] Fire Nearby [ ] Other _____

[ ] INVALID SAMPLE INFORMATION

Reason for Sample Invalidation

[ ] Vacuum lower than 5 psig
[ ] Vacuum higher than 20 psig
[ ] Sampling period out of range (<___ or >___ hours)
[ ] Other reasons: _____
[ ] Sampling equipment inoperative

Field Comments: _____

Sample Tracking

Action	Transfer Method (Check one)		Name & Initials	Date/Time
	Carrier	Person		
Released by Lab				
Received by Field				
Released by Field				
Received by Lab				

===FOR LABORATORY USE ONLY====

Lab Comments: _____

** = Calibrated Guage Pressure or Vacuum

07/13/07

Figure 6: **Sample Data Sheet**

RESIN SORBENT TUBE FIELD SAMPLE LOG SHEET

Project: Chloropicrin Pesticide Ambient Air Monitoring

Start Flow Set: 8.0 ±0.1 sccm End Flow Criteria: 8.0 sccm ±20%

Log #	Sample Name	Sampler ID Number	Date & Time Entry Example (6/14/08 13:42)		Counter		Mass Flow Meter Display		Corrected Average Flow	Comment Number	Weather K,P,C,F&R		Initials	
			Start	End	Start	End	Start	End			Start	End	Start	End

MFM Used #: _____ **Slope:** _____ **Intercept:** _____

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Weather Codes: K = Clear, P = Partly Cloudy, C = ≥67% Cloudy, F = Fog and R = Rain (any)

Figure 7: **Sample Data Sheet**

7.0 Quality Control

Quality control procedures will be observed to ensure the integrity of samples collected in the field. Certified transfer standards will be used to measure sample flow rates.

Each Summa canister will be assigned a field sample number that provides for identification of site, sample ID number, operator, and sample information as well as sample transfer information.

Field Spike (FS): A field spike will be prepared by the laboratory by injecting known concentrations of 1,3-D, CH_3Br and CH_3I into a cleaned and evacuated Summa canister. The sorbent tubes will be spiked with known concentrations of Cl_3CNO_2. All field spikes (15 for each sampling method) will be sampled in parallel with the primary samples. All field spikes will be installed, removed and handled identically to the other samples.

Field Blank (FB): A canister field blank will be a cleaned and evacuated Summa canister. A new sorbent tube will be used for the Cl_3CNO_2 field blank. Canister field blanks will be transported to the field, filled with zero air through the Tisch sampler and returned to the Laboratory. Sorbent tube field blanks installed and removed without sampling ambient air.

Collocated (CO): A collocated (side-by-side) air sampler will be operated exactly the same as the primary sampler and will be installed alongside the primary sampler.

Site/Sample Identification

The canister samples will be identified by the sample tracking sheet's laboratory identification number. The chloropicrin samples will be named accordingly as follows:

Site Naming Examples:
V-1 = Ventura sample 1 (65 samples V-1 through V-65)
SM-1 = Santa Maria sample 1 (65 samples SM-1 through SM-65)
SM-FS1 = Santa Maria field spike 1 (15 samples SM-FS1 through SM-FS15)
SM-FB1 = Santa Maria field blank 1 (15 samples SM-FS1 through SM-FS15)
SM-CO1= Santa Maria Collocated 1 (15 samples SM-CO1 through SM-CO15)

Following the quality control procedures listed above will ensure the quality and integrity of the samples collected in the field and will ensure accurate field and lab data collection.

8.0 Deliverables

8.1 Air Quality Surveillance Branch Deliverables

Within 90 days from receipt of the final results report from the Northern Laboratory Branch (NLB), AQSB will provide DPR with a report containing the following topics:

1) Sampling Protocol
2) Personnel Contact List
3) Site Photographs
4) Sample Summary Table
5) Field Sample Log
6) Laboratory Analysis Reports with calculations in electronic format
7) Disk containing electronic files of Report

In addition, the Special Purpose Monitoring Section (SPM) will prepare a project binder containing the above information. This binder will remain with SPM though available for viewing and review as requested.

APPENDIX A:

(MLD 058 Standard Operating Procedure for the Determination of Aromatic and Halogenated compounds in Ambient Air by Capillary Column Gas Chromatography/Mass Spectrometry)

APPENDIX B:

(Standard Operating Procedure for Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector).